Influence of BaZnCuO3 and BaZnCuO3/rGO on the thermal decomposition of AP and NTO

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Abstract

BaZnCuO3 (BZC) was synthesized using the sol-gel method. The BZC was incorporated in reduced graphene oxide (rGO) to produce BZC/rGO composite. The synthesized catalysts were characterized using Raman, powder X-ray diffraction (XRD), and Ultraviolet-visible (UV-Vis) analysis. The comparative effect of BZC and BZC:rGO composite was studied on the thermal decomposition of and 3-nitro-3H-1,2,4-triazol-5-one (NTO) and Ammonium Perchlorate (AP) using simultaneous Thermo-gravimetric technique (TG-DTA). BZC was a better catalyst for decreasing the thermal decomposition temperature and the thermo-kinetic parameters of both AP and NTO compared to BZC/rGO composite. BZC can reduce the thermal decomposition of AP and NTO by 121 oC, and 46 oC, respectively. The findings support BZC as a possible catalyst in the thermolysis of both NTO and AP.
INTRODUCTION

Materials such as ammonium perchlorate (AP), ammonium nitrate (AN), 3-nitro-3H-1,2,4-triazol-5-one (NTO), etc release a large amount of heat and gases during their decomposition. These large gases and heat released during the components’ decomposition are utilized for various applications such as destroying a target, propelling objects, etc. Changing the combustion or decomposition behavior of these materials influences the performance of explosive formulations or solid rockets propellants. Significant research has been conducted to identify alternative methodologies that focus on finding a synergistic impact between better stability and improved combustion and decomposition performance of high energetic materials. Various catalysts were utilized in the past for changing the thermal decomposition behaviors of high energetic materials, among which nanosize materials possess a slightly better catalytic effect for decreasing both thermal decomposition energy and decomposition of these materials. Nanosize materials have a size ranging below 100 nm and differ in properties compared to their bulk size material because of increased surface area and quantum confinement effects. e.g., a Study of Padwal and Varma show that the Fe$_2$O$_3$ nanoparticles exhibit a better effect for increasing the burning performance of solid propellants than micron size Fe$_2$O$_3$. The use of metal oxides, specifically 3d transition metal oxides were well studied for improving the thermal decomposition of high energetic materials. Recently, Perovskite type oxides (PTOs) have gained attention for improving the thermal performance of high energetic materials. PTOs have a general formula ABO$_3$ Where A site is occupied by a larger cation such as alkaline earth metals and B site is occupied by smaller cations such as transition metal cations. PTOs can catalyze reactions such as oxidation of CO, NO$X$, and reduction of CO$_2$, N$_2$, O$_2$, etc, which can potentially be produced during high energetic materials’ decomposition process and therefore, can potentially catalyze the decomposition of these materials. Use of metal oxides-reduced graphene oxide (r GO) or other carbon-based materials were known to improve the heat released during the decomposition of these high energetic materials as well as further reducing the decomposition temperature. This additional feature of metal oxides containing r GO could be assigned to r GO’s large surface support for various redox processes occurring during the decomposition.

In the present work, the catalytic effect of BaZnCuO$_3$(BZC) on the thermal decomposition of inorganic material AP and one heterocyclic energetic material NTO was investigated. Comparative studies of the
catalytic effect of pure BZC and BZC/rGO composite are also presented. BZC was synthesized using the sol-gel method and characterized using powder X-ray diffraction (XRD), Raman, and UV analysis.

EXPERIMENTAL PROCEDURES

2.1 Materials

Metal nitrate salts (Ba$^{2+}$, Zn$^{2+}$, and Cu$^{2+}$) were acquired from SRL Pvt. Ltd., India. GO was purchased from Merck, India. Go was thermally reduced at 350°C to rGO. NTO was synthesized using previously reported literature, AP was acquired from national chemicals.

2.2 Synthesis of BZC and BZC/rGO

BZC was synthesized using the previously reported sol-gel citrate-disodium ethylenediaminetraacetate (EDTA) method. Nitrate salts of metals Ba$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ were mixed in the 2:1:1 ratio followed by the addition of citric acid and EDTA in 2:1 mole ratio than of total metal content. The mixture was heated between 90-100 °C to form a gel. After the combustion of gel in the open air, the obtained residue was calcined at 700 °C for 4 hours to yield BZC. BZC was mixed with rGO in a 2:1 ratio in acetone followed by ultrasound irradiation for 40 minutes and drying in an oven to yield BZC/rGO composite.

2.3 Preparation of energetic material sample containing catalyst

The obtained BZC and BZC/rGO were mixed with NTO and AP to study their catalytic influence on the decomposition of AP and NTO. The composition of the samples and their labeling is depicted in Table 1.

Table 1. Samples for NTO and AP in the presence of different additives for thermal decomposition studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>Catalyst</th>
<th>Quantity of catalyst (% by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTO</td>
<td>N0</td>
<td>Nil</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>N1</td>
<td>BaZnCuO$_3$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>BaZnCuO$_3$/rGO</td>
<td>3</td>
</tr>
<tr>
<td>AP</td>
<td>A0</td>
<td>Nil</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>BaZnCuO$_3$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>BaZnCuO$_3$/rGO</td>
<td>3</td>
</tr>
</tbody>
</table>

APPARATUS

Powder XRD (Rigaku Ultima IV Powder X-Ray Diffractometer instrument equipped with a CuKα) and Raman spectroscopy (Jobin Yvon Horiba LabRam, HR800 laser sources with a λ=532 nm) were used for structural determination. The optical band gap energy was determined using UV-VIS analysis (Shimadzu UV-1800). Simultaneous TG-DTA data was collected at 10 °C min$^{-1}$ heating rate under a nitrogen gas flow of 150 ml min$^{-1}$ in an Alumina pan.

RESULTS AND DISCUSSION

4.1 Powder XRD

XRD spectrum of BZC and BZC/rGO is depicted in Figure 1. The XRD patterns of BZC were compared with that reported for Ba-based perovskite oxides. Major XRD peaks are obtained between 2θ=20 to 50 ° position. The Scherrer formula ($D=K\lambda/β \cos θ$) was used to the calculated crystalline size of the BZC and BZC/rGO. Where K is the constant (value=0.9). β, θ, D, and λ represents full-width-at-half-maxima, Bragg’s angle (2θ/2), size of the particle (nm), and wavelength (0.154 nm for Cu-Kα source), respectively. The crystalline size of BZC, and BZC/rGO was between 10-20 nm, confirming its nanosize. Both, BZC, and BZC/rGO exhibit similar XRD patterns.

Figure 1. XRD Spectrum of BZC and BZC/rGO

4.2 Raman analysis

Raman spectrum of BZC and BZC/rGO is given in Figure 2. The Raman spectrum of BZC exhibits a total of five peaks that appear between 200-700 cm$^{-1}$ with a Raman shift value of $^\sim$206, 281, 326, 430, and 694 cm$^{-1}$, respectively. The presence of peaks at these Raman shift values confirms the formation of perovskite-type BZC as reported by Chamorro et al. The composite addition of BZC/rGO composite exhibits similar peaks, however, the Raman bands between 200-500 cm$^{-1}$ were shifted to higher Raman shift region (blue shift, Figure 2) compared to BZC. Blueshift in BZC incorporating rGO could be because of a change in the chemical bond or interatomic bond force of the corresponding peak, as well.
as electron cloud movement.\textsuperscript{25} Disappearance of peak \textasciitilde 430 cm\textsuperscript{-1} in case of BZC/rGO composite could be because of the change in the bonding interaction of rGO with ZCB.

Figure 2. Raman Spectrum of BZ and BZC/rGO

4.3. Surface morphology

Figure 3 shows SEM images of BZC and BZC/rGO. The majority of particles in BZC were below 100 nm with an average of 94 nm size. Although some micron size particles were also visible. In BZC/rGO, the average particle size remains the same as that of BZC. The surface morphology of BZC and BZC/rGO composite is comparable. The bigger size disparity from the size determined by XRD might be due to the fact that XRD estimates the crystalline size, which varies from the size observed by SEM. Another aspect is that nano-scale particles tend to cluster due to their small size and large surface area, resulting in a secondary particle that is larger than the original particles.

Figure 3. SEM image of (a) BZC and (b) BZC/rGO

4.4 UV-Vis analysis

UV-Vis spectrum of ZCB/rGO, and Tauc’s plot\textsuperscript{26} for the indirect allowed transition of BZC and BZC/rGO composite are presented in Figure 4. Both BZC and BZC/rGO show characteristic absorption in the wavelength region of 200-500 nm. Upon incorporation of rGO, a bathochromic (red) shift in the wavelength region of 300-500 nm was observed. The wavelength maxima of BZC, 381 nm was shifted to 386 nm upon the incorporation of rGO. The optical band gap energy of BZC was 4.6 eV which was increased to 5.2 eV after the addition of rGO. The lower band-gap energy of BZC suggests that the electron can transfer quickly from the valence band to the conduction band compared to BZC/rGO composite.
Figure 4. UV-Vis spectrum (a), and corresponding Taucs’ plot (b) of BZC and BZC/rGO composite

4.5. Thermal decomposition studies

TG curves of various samples of AP and NTO are depicted in Figure 5. Thermal decomposition of N0, N1, and N2 samples takes place between 200-300 °C in a single step. The incorporation of additives in pure NTO causes the TG curve of NTO to shift towards the left side (i.e., lower temperature region). The order of thermal decomposition temperature was: N0>N2>N1. The TG curve reveals that the mass loss of N2 was 4 % higher and that in the case of N1 was 5 % lower compared to the pure N0 sample. As the mass ratio of the additive: pure NTO was 95:5, both the samples containing additives (i.e., N1 and N2) must have decomposed to yield a total mass loss that corresponds to 5 % lower than pure N0. However, the plausible explanation for higher mass loss in N1 could be that N1 must have catalyzed the residue that may have remained un-reacted when pure N0 was decomposed leading to greater mass loss than expected. The mass loss of N2 was 5 % lower that was because of the presence of the 5 % additive.

A0 decomposes in two steps; (i) between 250-330°C leading to a mass loss of 18 % called low-temperature decomposition (LTD) and (ii) between 331-450°C with a mass loss of 82 % called high-temperature decomposition (HTD). In the presence of the additives (A1 and A2), the TG curve of AP shifts to lower temperatures compared to A0. The TG curve of AP was changed drastically when the additives were incorporated. A2 decomposes in two steps at a lower temperature range, but the LTD step of A2 becomes more influential than LTD in A0. The mass loss in LTD of A2 was 13 % higher than in LTD of A0. The LTD step in A1 becomes the major decomposition step of AP with a mass loss of 90 % and other small decomposition takes place with only 7 % mass loss.

Figure 5. TG curve of NTO (a), and AP (b) with and without BZC, and BZC/rGO additive

DTA curves of A0-A2 and N0-N2 are depicted in Figure 6. N0, N1, and N2 decompose in a single exothermic event with a maximum curve temperature (T_m) of 276, 230, and 239 °C, respectively. DTA curve of N0 in the presence of additive was shifted to the left side, and the corresponding temperature value of DTA curves are depicted in Table 2. DTA curve of A0 exhibit three peaks, one endothermic peak ~242 °C corresponding to the phase transformation of AP from orthorhombic to cubic, and two exothermic peaks
belonging to the decomposition of AP. In the presence of additives, the endothermic peak of AP was varied by only 1-2° C, but LTD and HTD peaks of AP were affected drastically. LTD and HTD peaks of A2 were decreased by 21 and 71° C, respectively. In A1, two exothermic peaks of AP merge into a single exothermic peak at 292° C. The difference between onset temperature (T_o) and maximum temperature (T_m) also plays an important factor in determining the thermal performance of energetic materials (Table 2). [?]T of A1 and A2 was lower than A0, indicating the faster decomposition of AP in the presence of additives. N1 and N2 increase the [?]T of N0 by 3, and 26° C, respectively. The TG and DTA results suggest that BZC was a more suitable catalyst for influencing the thermal performance of both NTO and AP compared to BZC/rGO. The comparisons of previously reported additives (3 % by mass) on the thermal decomposition of AP is given in Table 3.27–30 From Table 3, it was evident that BZC containing AP composition decomposes at low temperature and hence, it can influence the burning rate properties of AP based propellants and formulations to compare to other catalysts with same content reported in Table 3.

**Figure 6. DTA curve of (a) NTO, and (b) AP with and without BZC, and BZC/rGO additive**

Table 2. DTA and TG data of AP, and NTO with and without catalyst (β=10° C min⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature (T_o) (°C)</th>
<th>Maximum temperature (T_m) (°C)</th>
<th>Difference (T_m-T_o) (°C)</th>
<th>TG mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0 (LTD)</td>
<td>289</td>
<td>312</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>A0 (HTD)</td>
<td>339</td>
<td>413</td>
<td>74</td>
<td>82</td>
</tr>
<tr>
<td>A1</td>
<td>272</td>
<td>292</td>
<td>20</td>
<td>90 ; 7</td>
</tr>
<tr>
<td>A2 (LTD)</td>
<td>278</td>
<td>292</td>
<td>14</td>
<td>31</td>
</tr>
<tr>
<td>A2 (HTD)</td>
<td>307</td>
<td>342</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>N0</td>
<td>255</td>
<td>276</td>
<td>21</td>
<td>78</td>
</tr>
<tr>
<td>N1</td>
<td>206</td>
<td>230</td>
<td>24</td>
<td>82</td>
</tr>
<tr>
<td>N2</td>
<td>202</td>
<td>239</td>
<td>37</td>
<td>75</td>
</tr>
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</table>

Table 3. Comparison of the the effect of various additives on the peak temperature of AP (3 % by mass)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shifting in HTD peak temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃/GO</td>
<td>378</td>
<td>27</td>
</tr>
<tr>
<td>BZC/rGO</td>
<td>342</td>
<td>Present work</td>
</tr>
<tr>
<td>Hollow mesoporous CuO</td>
<td>341</td>
<td>28</td>
</tr>
<tr>
<td>Co(OH)₂/rGO</td>
<td>320</td>
<td>30</td>
</tr>
<tr>
<td>MnCO₂O₄</td>
<td>297</td>
<td>29</td>
</tr>
<tr>
<td>BZC</td>
<td>292</td>
<td>Present work</td>
</tr>
</tbody>
</table>

**4.6 Thermo-kinetics parameters**

Kinetic parameters were calculated using the Coats-Redfern method[^31] to calculate the activation energy (E_a) and the pre-exponential factor (A).[^32] The results are presented in Table 4. The E_a of N0 and N2 were the same, indicating no effect of the BZC/rGO catalyst on the activation energy of NTO. However, the pre-exponential factor of the N2 was increased indicating a slower decomposition of N2 than N0. Both, the pre-exponential factor and activation energy of N1 were decreased indicating the faster decomposition of N1 than pure N0, indicating a good catalytic effect of BZC on the thermal decomposition of NTO than BZC/rGO. The activation energy of A0 for both HTD and LTD steps was increased when BZC/rGO (A2) additive was incorporated in AP, suggesting a negative effect of the additive on the kinetic parameters of AP. In A1, both the activation energy and the pre-exponential factor were in between that of LTD and HTD E_a and A of A0, this could be the result of the merging of the two exothermic peaks of A0 into a single peak in the case of A1 containing BZC additive. Various thermodynamics parameters were evaluated using Eq. (1) to (3).[^33] $H = E - RT$ (1) $G = E + RTln (\frac{K_A T}{\Delta})$
\[ S = \frac{H - G}{T} \]  

Where, \( R, T, E, G, H, \) and \( S \) represents the Universal gas constant (kJ mol\(^{-1}\) K\(^{-1}\)), temperature (K), activation energy, Gibbs free energy, enthalpy, and entropy, respectively. \( K_B \) and \( h \) represent Boltzmann constant and plank's constant, respectively. Thermo-kinetic data of the various samples are given in Table 3. N1 has the least value of thermo-kinetic parameters than N0 and N1, suggesting a very good catalytic effect of BZC on the thermal decomposition of NTO. A similar effect of BZC was observed on the thermo-kinetic parameters of AP. Hence, thermo-kinetics parameters also suggest that BZC was indeed a good catalyst than BZC/rGO for the thermal decomposition of both AP and NTO. High energy materials are assumed to undergo various oxidation and reduction reactions during their decomposition. BZC has lower bandgap energy than the BZC/rGO and hence, in BZC electron/hole transfer becomes easy during the decomposition and therefore BZC acts as a better catalyst than BZC/rGO.

Table 4. Kinetic and thermodynamic parameters obtained using Coats-Redfern method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_a ) [kJ/mol]</th>
<th>( A ) [min(^{-1})]</th>
<th>( ?G ) [kJ/mol]</th>
<th>( ?H ) [kJ/mol]</th>
<th>( ?S ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0</td>
<td>352</td>
<td>3.E+31</td>
<td>140</td>
<td>348</td>
<td>0.3788</td>
</tr>
<tr>
<td>N1</td>
<td>251</td>
<td>2.E+23</td>
<td>136</td>
<td>247</td>
<td>0.2203</td>
</tr>
<tr>
<td>N2</td>
<td>352</td>
<td>5.E+33</td>
<td>132</td>
<td>347</td>
<td>0.4209</td>
</tr>
<tr>
<td>A0 (LTD)</td>
<td>370</td>
<td>3.E+30</td>
<td>156</td>
<td>365</td>
<td>0.3573</td>
</tr>
<tr>
<td>A0 (HTD)</td>
<td>139</td>
<td>3.E+07</td>
<td>190</td>
<td>134</td>
<td>-0.0825</td>
</tr>
<tr>
<td>A1</td>
<td>209</td>
<td>8.E+15</td>
<td>159</td>
<td>204</td>
<td>0.0801</td>
</tr>
<tr>
<td>A2 (LTD)</td>
<td>661</td>
<td>4.E+58</td>
<td>149</td>
<td>656</td>
<td>0.8970</td>
</tr>
<tr>
<td>A2 (HTD)</td>
<td>346</td>
<td>9.E+26</td>
<td>162</td>
<td>341</td>
<td>0.2912</td>
</tr>
</tbody>
</table>

CONCLUSIONS

BZC was successfully synthesized using the sol-gel method. BZC/rGO composite was obtained by ultrasound-assisted technique. The crystalline size of both BZC and BZC/rGO falls into the nanoscale range. The thermal decomposition temperature of AP was reduced by 71 °C, and 121 °C in the presence of BZC/rGO, and BZC additive, respectively. NTO’s peak temperature was decreased by 37°C, and 46 °C in the presence of BZC/rGO, and BZC additive, respectively. The results suggest that BZC was a better additive for reducing the thermal decomposition temperature of both AP and NTO. The decrement in the thermo-kinetics parameters of AP and NTO in the presence of BZC also affirms the good catalytic influence of BZC on the thermal decomposition of AP and NTO. The order of influence of the catalyst on the thermal decomposition of AP and NTO was: BZC>BZC/rGO. The lower band-gap energy (4.6 eV) in BZC could have facilitated electrons transfer during the decomposition processes easily compared to the higher bandgap energy of BZC/rGO. Hence, BZC was good catalyst than BZC/rGO composite.

NOTES

The authors declare no competing financial interest.

DATA AVAILABILITY STATEMENT:

The data that supports the findings of this study are available in the Manuscript itself.

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REFERENCES


(23) Patterson, A. The Scherrer Formula for X-Ray Particle Size Determination. *Physical review* 1939, 56 (10), 978.


